

120-100-100-100
IN-46-71
111510-2881
073032

A SEARCH FOR EXTRATERRESTRIAL AMINO ACIDS IN POLAR ICE: A PROGRESS REPORT

Jeffrey L. Bada
Scripps Institution of Oceanography
University of California at San Diego
La Jolla, CA 92093

Karen L. F. Brinton
Scripps Institution of Oceanography

Gene D. McDonald
Scripps Institution of Oceanography

Xueyun Wang
Scripps Institution of Oceanography

Abstract - 1952

Fifteen polar ice samples—fourteen from Greenland and one from Antarctica—have been analyzed for the extraterrestrial amino acid α -aminoisobutyric acid (AIB) in an effort to estimate the flux of interplanetary organic material to the Earth's surface. Only one sample (Greenland GISP II, 4270–4440 years old) contains detectable amounts of AIB, apparently the signature of a transient delivery event. The maximum oceanic concentration of AIB from such an event would be less than 10^{-9} M.

INTRODUCTION

Extraterrestrial sources have been suggested as an alternative for the Earth-based synthesis of the organic compounds necessary for the origin of life (Oró 1961, Chyba and Sagan 1992). Such an alternative source of organics may have been necessary if the atmosphere of the early Earth was composed mostly of nonreducing

gases such as N_2 and CO_2 rather than CH_4 and NH_3 (Walker 1985, Kasting 1993, Kasting et al. 1993).

If extraterrestrial sources were important on the early Earth, they should still be supplying the Earth today with organic matter, although at a significantly reduced rate. Theoretical studies have indicated that organic molecules could be delivered to the Earth by cometary impactors (Chyba et al. 1990), but would be more likely to reach the Earth's surface intact if carried by micrometeorites and interplanetary dust particles (IDPs) with diameters in the tens to hundreds of microns (Anders 1989, Chyba and Sagan 1992). These particles can be collected in the stratosphere by aircraft, but the amount of material so far obtained by this method is much too low for detailed organic analyses. The only other alternative (besides in-orbit collection) is to attempt to detect exogenous organics at the surface of the Earth. Any extraterrestrial organic material that might reach the surface of the Earth, however, would be minuscule in comparison to terrestrial biogenic organics (see Table 1), and thus virtually impossible to detect in most terrestrial environments. The most pristine environment on Earth with respect to terrestrial organic matter is polar ice. Therefore, we have concentrated our search for extraterrestrial organic molecules—in particular extraterrestrial amino acids—on ice samples from Greenland and Antarctica.

We have analyzed several polar ice samples for the extraterrestrial amino acid α -aminoisobutyric acid (AIB). This molecule is the most abundant amino acid in carbonaceous meteorites (Cronin and Pizzarello 1983). Aside from a few fungal peptides (see, e.g., Mathew and Balaram 1983), it rarely occurs in the terrestrial biosphere. AIB has been found in association with the K-T boundary impactor (Zhao and Bada 1989), and routine and sensitive analytical techniques for this amino acid are available (Zhao and Bada 1995). AIB can therefore be used as a marker for the presence of extraterrestrial organics on the Earth.

TABLE 1. Amino Acids on the Earth

	Carbon (10^{15} g)	Amino Acid Content	Amino Acids (10^{15} g)
Biosphere	600–800	< 10%	< 100
Polar Ice	3*	1 ppb [†]	0.03
Seawater Organics	2000–3000	1%	20–30
Soil Organics	1000	< 1%	< 10
Sediments			
Organics	3×10^7	0.02–1%	6000–300,000
Carbonates	10^8	20–300 ppm	1000–30,000

* Total ice = 2.9×10^{19} kg; organic carbon = $100 \mu\text{g C kg}^{-1}$.

† Total amino acid content of polar ice.

METHODS

All ice core samples weighed between 3 and 7 kg. Each sample was melted and evaporated to dryness, and the residue redissolved in approximately one ml of double-distilled H₂O. Aliquots were then taken and derivatized by the o-phthaldialdehyde/N-acetyl cysteine (OPA/NAC) technique. The derivatives were separated by reverse-phase high-performance liquid chromatography (HPLC) with fluorescence detection and identified by comparison of retention times with authentic standards (Zhao and Bada 1995). Aliquots were also taken and hydrolyzed in double-distilled 6N HCl at 100°C for 24 hours. These aliquots were then dried and analyzed as above.

The sample believed to contain AIB was reacted with ninhydrin in pH 2.5 citrate buffer at 100°C for 5 minutes (Brinton and Bada 1994). The solution was then passed through an activated charcoal column, dried and analyzed as above.

RESULTS

We have analyzed one sample from the Allan Hills region of Antarctica, twelve samples from the Greenland Dye 3 site and two from the Greenland GISP II site. These ice samples range in age from approximately 100 to 100,000 years before present (BP). The levels of AIB present in these samples are shown in Table 2. AIB was not detected in the Antarctic sample, any of the twelve Dye 3 samples, or the 6000 year old GISP II sample. The levels in Table 2 are upper limits based on the detection limits of the OPA/NAC technique.

AIB was detected in one sample from the GISP II drilling site in Greenland (Table 2). The chromatographic retention time of the peak identified as AIB is consistent with that of an authentic standard. In addition, the yield of this peak increases between one

TABLE 2. *Extraterrestrial Amino Acids in Polar Ices*

	<i>Number of Samples</i>	<i>Age</i>	<i>ppb AIB</i>
Antarctic		~ 10 ⁵ yr BP	< 0.0005 (unhyd)
Allan Hills	1		< 0.002 (hydrol)
Greenland			
Dye 3	12	1860–1930 AD	< 0.001 (unhyd) < 0.001 (hydrol)
GISP II	2	4270–4440 yr BP	0.35 (unhyd) 0.11 (hydrol)
		6010–6240 yr BP	< 0.001 (unhyd)

minute and 15 minute derivatizations with the OPA/NAC reagent, as does the yield of authentic AIB but not the yields of protein amino acids (Zhao and Bada 1995). Reaction with ninhydrin results in approximately 25% destruction of the putative AIB (again consistent with authentic standards; Brinton and Bada 1994), while the protein amino acids in the sample were almost completely destroyed. Since the behavior of the AIB peak is consistent with authentic AIB in these respects, we conclude that AIB is present in the 4270–4440 yr BP GISP II sample.

Although AIB is rare in the biosphere, contamination in ice samples cannot be completely dismissed. The amount of AIB detected in the sample does not increase with HCl hydrolysis, indicating that all the AIB present is in the free amino acid form rather than in peptide residues. This argues against terrestrial biological contamination as a source of the AIB detected in the GISP II sample. In addition, a second, older sample of GISP II ice does not contain detectable levels of AIB (see Table 2). Because both samples were drilled at the same time using the same techniques, AIB contamination from the drilling or sample handling procedures at the GISP II site can be ruled out.

DISCUSSION

Anders (1989) has estimated the annual flux of intact organics from IDPs to the Earth as $3 \times 10^8 \text{ g yr}^{-1}$. Assuming that IDP organic carbon is less than 1% extraterrestrial amino acids (AIB and isovaline), the expected concentration of extraterrestrial amino acids (ETAA) in Greenland ice would be $< 2 \times 10^{-11} \text{ g kg}^{-1}$ ice, and the ETAA concentration in Antarctic ice would be $< 1 \times 10^{-10} \text{ g kg}^{-1}$. The measured upper limits for ETAA in Antarctic and Greenland Dye 3 ice, as well as for the 6000 yr BP GISP II sample, are consistent with and certainly no higher than the expected levels based on IDP flux. The 4300 yr BP GISP II sample, however, contains AIB at a concentration three orders of magnitude greater than the expected levels and that determined in the other ice samples analyzed.

If this AIB is extraterrestrial, it would seem to be a marker for a transient event that delivered extraterrestrial organics to the Earth around 4300 years ago. Failure to detect ETAA in the other samples listed in Table 2 suggests that the baseline flux of extraterrestrial organics at the Earth's surface is at or below the level estimated by Anders (1989). Studies of micrometeorite size distributions in Greenland ice (Maurette et al. 1987) indicate that the 3–7 kg samples analyzed for ETAA should contain an average of only 1–7 micrometeorites of around 100 μm diameter. The amount of AIB present in the GISP II sample is much too large to come from a few 100 μm particles, further suggesting that this AIB is the signature of a transient event.

If these data are the signature of a global ETAA delivery event around 4300 years ago, its astrophysical nature is not clear. The amount of AIB delivered globally by this event can be calculated from the measured AIB level in the GISP II sample, assuming a concentration of AIB similar to that of the Murchison meteorite (10 ppm), and assuming that the extraterrestrial material was deposited over the entire 170 year time span of the sample. Such calculations suggest an impactor with a diameter of around 7 km, large enough to have left lasting evidence of its arrival. If the extraterrestrial material was deposited completely in one year, the size of the impacting object is reduced to around one km. If the event delivered material only to the Greenland ice sheet rather than globally, the impactor size could be as small as 200 m. A collision between the Earth and a 200 m object would be expected to occur once every 10^3 – 10^4 years, while the impact of a one km object would occur once every 10^5 years (Chapman and Morrison 1994). A close approach of the Earth by a long-period comet, and the deposition on the Earth of cometary dust by a mechanism similar to that suggested for the K-T boundary amino acids (Zahnle and Grinspoon 1990) might be a plausible explanation. The ETAA flux in this case would be expected to gradually decrease to background levels over time.

It should be noted that the delivery event represented by the AIB in the GISP II sample, even if a global one, would result in a maximum oceanic AIB concentration of 3×10^{-11} M. Even if the AIB were initially concentrated in the upper 100 m of the ocean, the level of AIB would be only around 10^{-9} M. Such concentrations of extraterrestrial organic molecules would probably not be significant in prebiotic organic chemistry on the early Earth.

We hope to determine the areal extent of ETAA delivery from this event by analyzing ice core segments of the same age as the GISP II sample from other locations in either Greenland or Antarctica. Carbon isotope analysis may also be useful in confirming the extraterrestrial origin of the AIB detected, although the small amounts of amino acids involved may be at or below the limits of isotopic analysis.

ACKNOWLEDGMENTS

The authors thank Harmon Craig for the Dye 3 and Allan Hills samples, Tom Woiwode for help in collecting the GISP II samples, and the NASA Specialized Center for Research and Training in Exobiology at the University of California at San Diego for support.

REFERENCES

ANDERS, E. (1989), "Pre-biotic Organic Matter from Comets and Asteroids," *Nature* 342: 255-257.

BRINTON, K.L.F., AND J.L. BADA (1994), "The Use of the Ninhydrin Reaction for the Elimination of Protein Amino Acids in Cosmogeochemical Samples," *Origins of Life* 24: 125-126.

CHAPMAN, C.R., AND D. MORRISON (1994), "Impacts on the Earth by Asteroids and Comets: Assessing the Hazard," *Nature* 367: 33-40.

CHYBA, C., AND C. SAGAN (1992), "Endogenous Production, Exogenous Delivery and Impact-Shock Synthesis of Organic Molecules: An Inventory for the Origins of Life," *Nature* 355: 125-132.

CHYBA, C.F., P.J. THOMAS, L. BROOKSHAW, AND C. SAGAN (1990), "Cometary Delivery of Organic Molecules to the Early Earth," *Science* 249: 366-373.

CRONIN, J.R., AND S. PIZZARELLO (1983), "Amino Acids in Meteorites," *Adv. Space Res.* 3: 5-12.

KASTING, J.F. (1993), "Earth's Early Atmosphere," *Science* 259: 920-926.

KASTING, J.F., D.H. EGGLER, AND S.P. RAEBURN (1993), "Mantle Redox Evolution and the Oxidation State of the Archean Atmosphere," *J. Geol.* 101: 245-257.

MATHEW, M.K., AND P. BALARAM (1983), *Mol. Cell. Biochem.* 50: 47-52.

MAURETTE, M., C. JEHANNO, E. ROBIN, AND C. HAMMER (1987), "Characteristics and Mass Distribution of Extraterrestrial Dust from the Greenland Ice Cap," *Nature* 328: 699-702.

ORÓ, J. (1961), "Comets and the Formation of Biochemical Compounds on the Primitive Earth," *Nature* 190: 389-390.

WALKER, J.C.G. (1985), "Carbon Dioxide Cycle on the Early Earth," *Origins of Life* 16: 117-127.

ZAHNLE, K., AND D. GRINSPOON (1990), "Comet Dust as a Source of Amino Acids at the Cretaceous/Tertiary Boundary," *Nature* 348: 157-160.

ZHAO, M., AND J. BADA (1989), "Extraterrestrial Amino Acids in Cretaceous/Tertiary Boundary Sediments at Steens Klint, Denmark," *Nature* 339: 463-465.

ZHAO, M., AND J. BADA (1995), "Determination of α -Dialkylamino Acids and Their Enantiomers in Geological Samples by High-Performance Liquid Chromatography after Derivatization with a Chiral Adduct of α -Phthaldialdehyde," *J. Chromatog. A* 690: 55-63.

peruse
that co
sary fo
time fo
compo
organic
life on

or the
are the
thing !
comet
bathed
radiati
are des